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TIVE TIME LAGS IN THE ELECTRIC BREAKDOWN OF LIQUID HYDROCARBONS

by

R. W. Crowe

ort No. 55-RL-1432

November 1955

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Published by
Research Information Services Section
The Knolls
Schenectady, New York

ABSTRACT

Recent investigations of the time dependence of electrical breakdown in liquid hydrocarbons have led to a disagreement regarding the influence of molecular structure upon the formative time lag. This report represents an attempt to resolve the discrepancy, and to determine if possible the significance of the time lag in the breakdown process. The experiments involve the application of rectangular pulses of voltage of variable duration and amplitude to the liquids between hemispherical electrodes.

The results of the investigation show definitely that the formative time lag is insensitive to changes in the molecular weight of the hydrocarbon liquid. Consequently, it cannot be associated with the time required for positive ions to cross the spark gap, as has been suggested by recent investigators. Its characteristic dependence upon the electrode separation, however, suggests that it may be a measure of the transit time of an electron or an electron avalanche. This observation is consistent with a streamer-type mechanism of breakdown, not unlike that proposed for sparking in gases.

FORMATIVE TIME LAGS IN THE ELECTRIC BREAKDOWN OF LIQUID HYDROCARBONS

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INTRODUCTION

The physical processes operative in the development of electrical breakdown in a dielectric are often reflected in the time interval between the application of a d-c voltage and the appearance of the spark. This time may include both the time required for a free electron to appear at or near the cathode (statistical time lag) and the time required for the spark to develop after such an electron begins to move toward the anode under the influence of the electric field (formative time lag). It is the latter that provides the most information about the breakdown process.

The formative time lag to breakdown can be studied experimentally only if the statistical contribution is made an insignificant part of the total lag. In gas breakdown, this is accomplished by illuminating the cathode with ultraviolet light. In liquids, on the other hand, it is apparently taken care of automatically by cold emission of electrons from the cathode at the relatively high electric fields necessary to cause breakdown.

In 1951, Edwards⁽¹⁾ found that the formation time of spark breakdown was approximately the same for a wide variety of liquids, the exact value depending on the electrode separation. In a more recent paper, Goodwin and Macfadyen⁽²⁾ have reported that the time lag to breakdown in hydrocarbon liquids increases with increasing molecular chain length and liquid viscosity. In fact, the observation of a linear dependence of time lag upon the time required for positive ions to cross the spark gap was used by these investigators as evidence that the accumulation of a positive space charge near the cathode is an important feature of the breakdown process in liquids.

A preliminary investigation, designed to resolve the above discrepancy, was carried out recently in this Laboratory. (3) The time dependence of breakdown was measured at a constant electrode separation for two hydrocarbon liquids (<u>n</u>-hexane and <u>n</u>-nonane) of different molecular weight and viscosity. Although the electric

strengths of the two liquids were noticeably different, the time required for the spark to develop remained essentially unchanged. This observation was in agreement with the earlier findings of Edwards.

In this report we present the results of a more complete study of formative time lags in the breakdown of liquid hydrocarbons. The measurements have been extended to include other members of the hydrocarbon series, and the influence of electrode separation upon the time lag has been investigated in detail.

EXPERIMENTAL TECHNIQUES

The test cell used for the measurements reported here was the same as that described in earlier work. (3) The electrodes were mechanically polished hemispheres of stainless steel (one inch in diameter). The hydrocarbon liquids were of the <u>pure</u> grade (99 mole per cent minimum) as obtained from the Phillips Petroleum Company. Additional purification was accomplished by the techniques described earlier. (3)

The breakdown measurements were made by applying single rectangular voltage pulses of various durations (see Fig. 1) and of gradually increasing amplitude to the liquids until breakdown occurred. The dependence of electric strength upon pulse duration provides a measurement of the formation time of the spark. It has already been demonstrated that a high degree of precision and reproducibility can be realized by the use of these techniques. Consequently, it was seldom necessary to repeat breakdown measurements for a given liquid, pulse duration, and gap spacing more than ten times to obtain a reliable value of the electric strength.

EXPERIMENTAL RESULTS AND DISCUSSION

During the course of this investigation we have observed, as have others, (1,2,4) that the electric strength of a liquid hydrocarbon is independent of the duration of the applied voltage, provided the pulse used is longer than some critical value, τ_0 . In other words, if pulses of duration greater than τ_0 are used, breakdown invariably occurs when a time equal to τ_0 has elapsed. If, on the other hand, pulses of duration less than τ_0 are applied to the liquid, the electric field required for breakdown increases sharply, and the entire pulse duration is a measure of the formative time lag. A typical example of this behavior is shown in Fig. 2. The time, τ_0 , then, represents the time required for the spark to develop when the applied field is just equal to the threshold for electrical breakdown, E_s .

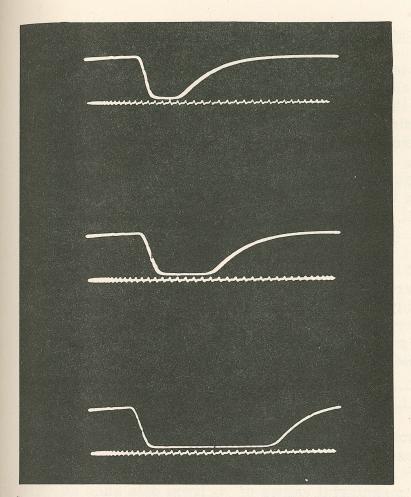


Fig. 1 Photograph
showing three typical
voltage pulses used
for breakdown measurements. Each spike
on the marker sweep
represents 0.1 microsecond.

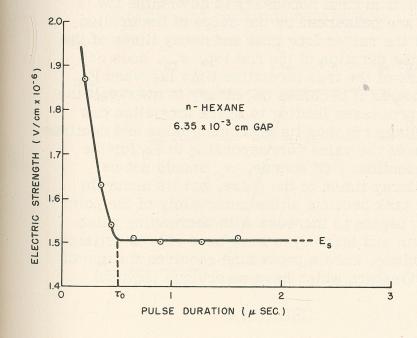


Fig. 2 Typical curve showing the dependence of the electric strength of a hydrocarbon liquid upon pulse duration.

The Dependence of Time Lag Upon Electrode Separation

The nature of the dependence of the formative time lag, τ_f , for a given liquid upon the electrode separation, δ , should provide valuable information about its significance in the breakdown process. Both Edwards(1) and Goodwin and Macfadyen(2) have observed that $\tau_0(\tau_f \text{ at } E_s)$ for liquid hydrocarbons increases in a fairly regular manner with increasing δ . However, it has already been pointed out that the latter authors do not agree with our own observations and those of Edwards regarding the influence of molecular size upon the time lag. Consequently, it seemed advisable to reinvestigate the variation of τ_f with δ using our own experimental techniques.

The dependence of the electric strength of \underline{n} -hexane upon pulse duration and electrode separation is shown in Fig. $\overline{3}$. Note that the time lag increases noticeably as δ becomes larger. Such a dependence suggests immediately that τ_f might be associated, at least in part, with the time required for some charge species to cross the spark gap. If such is the case, it should be possible to show that

$$\tau_f = \delta/\mu E_m, E_m > E_s,$$
 (1)

where μ represents the mobility of the charge species in question, and E_m is the measured breakdown field.

In order to obtain meaningful values of τ_f from data such as that shown in Figs. 2 and 3, it is first necessary to determine the extent to which the results are influenced by the shape of the applied voltage pulse. Because of the rather long rise and decay times of the pulse (see Figs. 1 and 4), the duration of the flat top, τ_{m} , does not provide an accurate measure of the true formative time lag when Em is greater than Es. As soon as it becomes necessary to over-volt the gap to realize breakdown, processes leading to spark formation can begin before the applied voltage reaches its maximum value and continue until the pulse decays again to the value corresponding to Es for the particular gap spacing in question. Of course, τ_0 should not be influenced by the rise and decay times of the pulse, but its accurate determination is a difficult task because of the uncertainty of the point where the electric strength begins to increase with decreasing pulse duration. Although Goodwin and Macfadyen have been able to estimate to by a curve-fitting technique, such a procedure requires the use of a number of adjustable parameters which have no obvious physical significance.

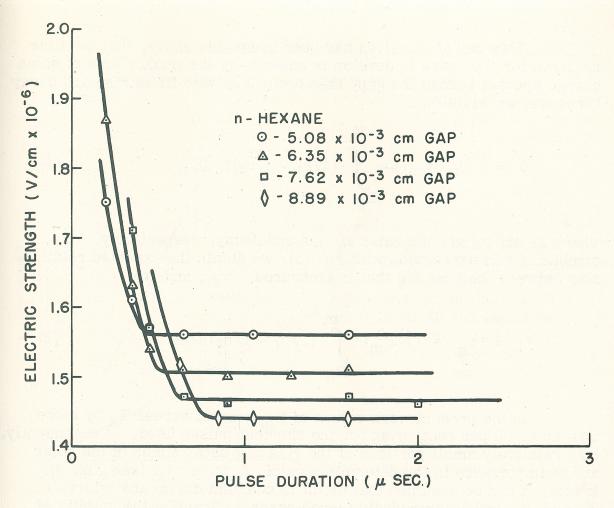


Fig. 3 The dependence of the electric strength of \underline{n} -hexane upon pulse duration and electrode separation.

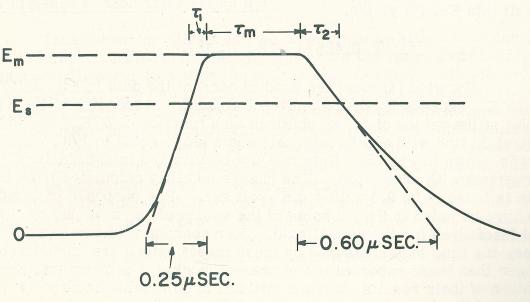


Fig. 4 Schematic representation of a typical voltage pulse used for breakdown measurements.

If we can assume, as has been suggested above, that the time required for the spark to develop is essentially the transit time of some charge species across the gap, then for pulses with finite rise and decay times we can write that

$$\delta = \mu E_{\rm m} \tau_{\rm m} + \mu \int_{E_{\rm S}}^{E_{\rm m}} (1/r_1 - 1/r_2) E dE,$$
 (2)

where r_1 and r_2 are the rates of rise and decay, respectively. By combining this expression with Eq. (1), we obtain the expected relationship between the time lag that is measured, τ_m , and τ_f ;

$$\tau_{f} = \tau_{m} + (1/E_{m}) \int_{E_{S}}^{E_{m}} (1/r_{1} - 1/r_{2}) E dE.$$
 (3)

In the present work values of E_m seldom exceed E_s by more than about 30 per cent, even for the shortest pulses used. Consequently, only relatively small portions of the rise and decay times of the pulse are of importance in the determination of τ_f from τ_m (see Fig. 4). In fact, it can be assumed that dE/dt is constant during the intervals τ_1 and τ_2 without introducing much error. Granting the validity of such an approximation, we find from an examination of Fig. 4 that $r_1 = E_m/0.25$ and $r_2 = -E_m/0.60$ volts/cm μ sec. Introduction of this result into Eq. (3) yields,

$$\tau_{\rm f} = \tau_{\rm m} + 0.425 [1 - (E_{\rm s}/E_{\rm m})^2].$$
 (4)

Equation (4) has been used to correct the data in Fig. 3 for which E_m exceeds E_s by a significant amount. According to Eq. (1), a plot of the values of τ_f so obtained as a function of δ/E_m should yield a straight line with a zero intercept and a slope equal to $1/\mu$. Such a plot is shown in Fig. 5. Note that the results are in satisfactory agreement with prediction. The charge mobility calculated from these data is found to be 9.1 x 10^{-3} cm²/volt sec. For purposes of comparison, we have included in Fig. 5 some of the values of τ_0 obtained by Goodwin and Macfadyen for the same liquid. For reasons unknown to us at this time, the time lags measured by these investigators are considerably longer than those reported in the present work. Furthermore, the scatter of their results makes it difficult to determine accurately the nature of the dependence of τ_0 upon $\delta/E_{\rm S}$.

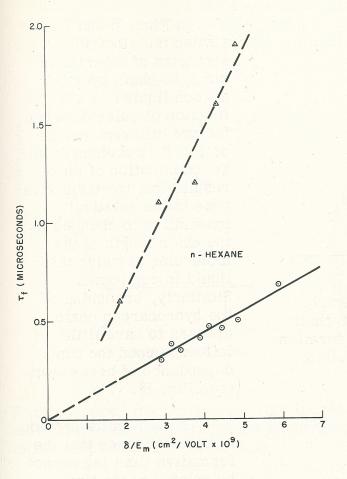


Fig. 5 The dependence of the true formative time lag upon the ratio $\delta/E_{\rm m}$ for <u>n</u>-hexane. The triangles represent data taken from the work of Goodwin and Macfadyen (see Reference 2).

The Influence of Molecular Structure

Thus far in the discussion we have made no attempt to identify the charge species that presumably must cross the spark gaps before breakdown will occur in a liquid hydrocarbon. Because both electrons and positive ions may be present or produced during breakdown, two such species must be considered. It has already been mentioned that one of the more important observations made by Goodwin and Macfadyen was that the formative time lag in the breakdown of liquid hydrocarbons increased rapidly with increasing molecular weight of the liquid. In fact, this observation led to the development of a theory of electrical breakdown in liquids which involved the movement of positive ions, produced by collision ionization, across the gap. However, because this behavior was not observed in our own preliminary investigations, (3) it appeared worthwhile to extend the measurements to include a wider variety of hydrocarbon liquids.

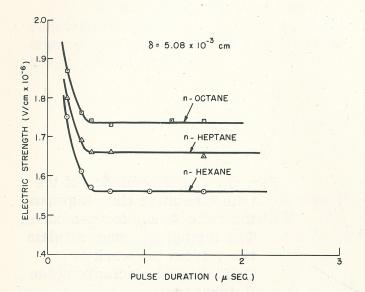


Fig. 6 The dependence of the electric strengths of a series of straight-chain hydrocarbon liquids upon pulse duration for an electrode separation of 5.08 x 10⁻³ cm.

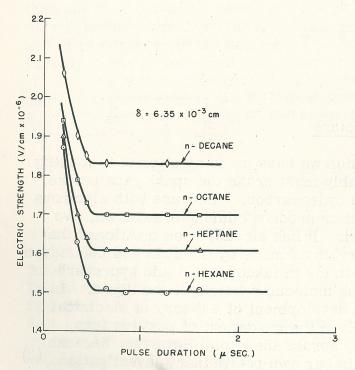


Fig. 7 The dependence of the electric strengths of a series of straight-chain hydrocarbon liquids upon pulse duration for an electrode separation of 6.35 x 10⁻³ cm.

-8-

In Figs. 6 and 7 are plotted the electric strengths of a series of straight-chain hydrocarbon liquids as a function of pulse duration for two different values of b. It is obvious from an examination of these results that the formative time lag is relatively insensitive to changes in the chain length of the molecules of which the liquid is composed. Similarly, branching of the hydrocarbon chain appears to have little influence upon the time dependence of breakdown (see Fig. 8).

These results provide definite evidence that the formative time lag cannot be related to the time required for positive ions to traverse the spark gap or any significant fraction thereof. According to the mobility measurements of Adamczewski, (5) a time of at least 5 microseconds is required for a positive ion of n-hexane to cross a gap of 6.35 \times 10⁻³ centimeters if the applied field is equal to E. In the case of n-octane, the ion transit time is at least 12 microseconds. These times are far in excess of the measured formative time lags for these liquids.

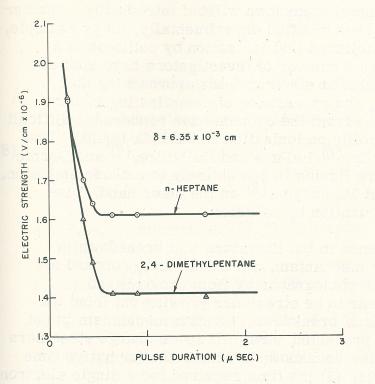


Fig. 8 The dependence of the electric strengths of two isomers of heptane upon pulse duration.

Furthermore, the ion transit time increases rapidly with increasing molecular size, while the time required for breakdown to develop is not influenced by such a change.

On the basis of the above observation, it seems more reasonable to assume that the mobility calculated from the data in the last section is that of an electron or an electron avalanche in n-hexane, and that if positive ions are produced, they remain essentially stationary during the build-up process. At first glance, it might appear that a value of 9.1 x 10⁻³ cm²/volt sec for the mobility of an electron in n-hexane is unexpectedly small when compared with that (8.27 x 10⁻⁴ cm²/volt sec) of the positive ion. It is likely, however, that electrons in a liquid spend at least part of the time trapped or attached to neutral hydrocarbon molecules and only occasionally break away as free electrons under the influence of an intense electric field. Under these circumstances, the measured mobility might be expected to be somewhat smaller than that of a completely free electron, and yet relatively insensitive to variations in molecular size.

In the foregoing discussion, we have said very little about the actual mechanism of electrical breakdown in liquid dielectrics. The results presented here do not provide us with sufficient information to

develop a general theory of liquid breakdown without introducing a number of assumptions that have not been verified experimentally. For example, it has never been clearly established that ionization by collision is a contributing factor. Although a number of investigators have studied the conduction process in liquids at electric fields approaching that required to cause breakdown, the appearance of complicating factors such as cold electron emission from the cathode have rendered it difficult to assess the importance of collision ionization in the bulk liquid. The experiments of Baker and Boltz, (6) LePage and DuBridge, (7) and Dornte (8) suggest that conduction in pure liquids is due entirely to cathode emission. Nikuradse (9) and Goodwin and Macfadyen, (2) on the other hand, have obtained some evidence of ionization by collision.

There is some evidence in the literature that breakdown in liquids occurs by a streamer mechanism, not unlike that proposed for breakdown in gases. (10) The photographs by Komelkov (11) and Washburn (12) show what appear to be streamers growing out from the anode during the latter stages of breakdown. Such a mechanism is not inconsistent with the results presented here. If space charge streamers do play an important role in the breakdown process, the formative time lag should consist of two parts: (1) the time required for a single electron avalanche to produce sufficient field distortion near the anode to favor the growth of the streamer, and (2) the time required for the streamer to cross the gap. Because the latter process is extremely rapid, the main part of the time lag should involve the transit time of the electron avalanche, as we have suggested earlier.

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